Indian J. Phys. **43**, 665–673 (1969)

On the ultraviolet band system of silicon monoxide

By Jagadish Singh, K. N. Upadhya and K. P. R. Nair

Department of Spectroscopy, Banaras Hindu University, Varanasi. 5

(Received 9 *August* 1968—*Revised* 24 *July,* 23 *September and* 20 *November* 1969*)*

Plate 9

The ultraviolet bands of SiO have been obtained in transformer discharge and the rotational analyses of (0,0), (2,0), (3,0), (4,0), (4,1) and (5,1) bands have been done from plates taken on the third order of a 10.6 meter concave grating spectrograph. The molecular constants derived are as follows :

$B_e'' = 0.7271\ \mathrm{cm}^{-1}$ $\qquad B_0' = 0.6305\ \mathrm{cm}^{-1}$

$r_e'' = 1.508\ \text{Å}$ $\qquad r_0' = 1.619\ \text{Å}$

In addition several perturbations have been obtained in the upper state.

Introduction

The rotational analysis of the ultraviolet band system of silicon monoxide lying in the region 2000Å – 3000Å was done by Saper (1932) and the transition involved was found to be a $^1\pi - {}^1\Sigma^+$ type transition analogous to the fourth positive system in CO molecule. He had also observed perturbations in the upper state, but his analysis was limited only to $v' = 0$ and 1 levels. Later Lagerqvist & Uhler (1953) analysed seven bands and obtained perturbations in the $v' = 2$ level also. However, they did not analyse bands involving higher vibrational levels in the upper state. Hence it was thought desirable to extend the analysis to bands involving higher vibrational levels in the upper state and to investigate the perturbations in those levels. Previous workers obtained the spectrum from an arc source and photographed the spectra on a 21 ft concave grating spectro- graph. They have also discussed in detail the nature of perturbing states and their constants. We have now succeeded in getting the bands with higher vibrational levels in the upper state and a number of perturbations in the different vibrational levels of the upper electronic states have been detected.

Experimental

The bands were obtained in a π—type discharge tube through the flowing vapour of $SiCl_4$. Under this condition the bands due to SiO molecule are developed well and hence other possible sources were not attempted. The bands were photographed in the third order of the 10.6 meter concave grating spectrograph with a disperson of 0.23 Å/mm. Iron arc spectrum was used as the comparison spectrum. A chlorine gas filter was used to cut off the second order spectra. Exposure of nearly 10 hours was sufficient to photograph the spectra with good intensity. The (0,0), (2,0), (3,0), (4,0), (4,1) and (5,1) bands were measured and analysed. The (2,0) band was included since new perturbations were detected.

Rotational Analysis

The bands show three series of lines with an intense Q branch showing a transition of the type $^1\pi - {}^1\Sigma^+$ (figure 1). In (4,1) band only two series of lines are observed in which the series are supposed to be Q and R branch. Such cases are also observed by Lagerqvist in the cases of (1,1) and (0,4) bands. Combination differences were obtained with bands having common lower vibrational levels. The rotational constants for these levels were obtained by plotting $\Delta_2 F(J)/(J+\frac{1}{2})$ *versus* $(J+\frac{1}{2})^2$ as given by Herzberg (1950). For common levels mean $\Delta_2 F(J)$ values were taken. The constants for the upper perturbed levels were determined from the ΔB values obtained from the graphs,

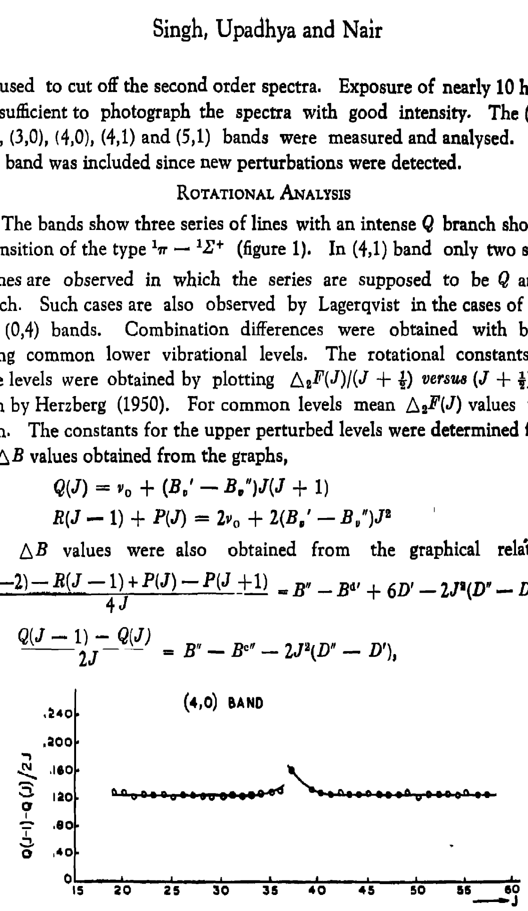
$$Q(J) = \nu_0 + (B_v' - B_v'')J(J+1) \tag{1}$$

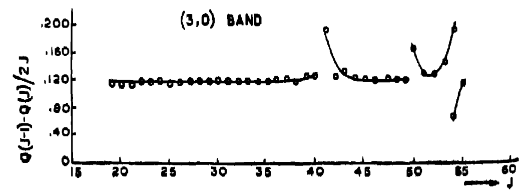
and $$R(J-1) + P(J) = 2\nu_0 + 2(B_v' - B_v'')J^2 \tag{2}$$

ΔB values were also obtained from the graphical relations

$$\frac{R(J-2) - R(J-1) + P(J) - P(J+1)}{4J} = B'' - B^{c\prime} + 6D' - 2J^2(D'' - D') \quad (3$$

and $$\frac{Q(J-1) - Q(J)}{2J} = B'' - B^{c\prime\prime} - 2J^2(D'' - D'), \tag{4}$$





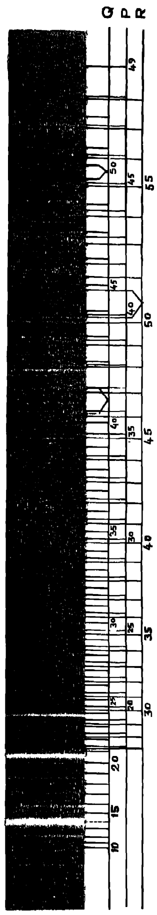


Figure 1. 3,0 Band

the intercept of the graph at $J = 0$ giving the $\triangle B$ value (Gerö 1935). The analysis and the J assignments of the individual lines are given in table 1.

TABLE 1.
(2,0) band

J	$Q(J)$	$P(J)$	$R(J)$	J	$Q(J)$	$P(J)$	$R(J)$
5	44306.19			36	60.57	14.92	06.81
6	04.19			37	52.22	10.24 03.73	199.0
7	02.54	44292.71					
8	00.34	89.94		38	43.59	098.40	91.32
9	297.67	86.51		39	34 86	87.74	83.62
10	95.42	83.09		40	25.92	77.75	76.92
11	92.71	79.37		41	16.69	67.42	68.24
12	89.94	75.33		42	07.33	56.87	59.79
13	87.37	71.09		43	097.60	45.92	51.31
14	84.15	66.88		44	87.74	34.85	42.65
15	80.92	62.33		45	77.75	23.39	33.71
16	77.24	57.61	44298.14	46	67.42	11.87	24.73
17	73.57	52.72	95.42	47	56.87	00.02	14.92
18	69.59	47.76	92.71	48	45.92	43988.00	05.63
19	65.33	42.47	89.94	49	34.85	75.61	095.93
20	60.94	36.67	86.51	50	23.39	63.32	85.64
21	56.26	30.67	83.09	51	11.87	50.52	75.65
22	51.34	24.41	79.37	52	00.02	37.64	64.94
23	46.29	17.88	75.33	53	43988.02	24.49	55.10
24	40.88	11.38	71.09	54	75.61	11.24	43.19
25	35.12	04.41	69.59 66.88	55	61.62	97.49	32.02
26	29.41	197.21	63.86	56	56.05 43.80	83.72	20.36
27	23.25	91.33 89.19	58.85	57	40.84	69.74	08.87
				58	26.88	54.86	43996.82
28	17.02	83.62	53.61	59	13.23	41.11	84.71
29	10.09	76.10	47.76	60	899.40	25.85	—
30	03.92	63.24	42.47	61	85.97	10.87	59.35
31	197.21	59.79	36.57	62	71.33	—	46.16
32	94.26	51.10	36.37	63	56.77		32.64
33	85.12	42.65	24.41	64	41.11		
34	76.17	33.71	17.88	65	25.85		
35	68.76	24.76	15.78 09.23				

TABLE 1. (Continued)

(3,0) band

J	$Q(J)$	$P(J)$	$R(J)$
9	45112.2		
10	09.94		
11	07.20		
12	04.86		
13	01.17		45119.12
14	—	45080.98	17.05
15	094.68	76.61	14.14
16	90.76	—	—
17	86.75	66.10	08.58
18	82.42	59.69	04.50
19	78.01	54.91	02.37
20	73.04	49.29	098.84
21	68.56	43.14	94.78
22	63.28	36.65	90.76
23	57.82	30.02	86.85
24	52.05	23.30	82.42
25	46.37	16.33	78.01
26	40.24	08.87	73.40
27	33.89	01.09	68.56
28	27.26	44993.76	63.28
29	20.48	85.50	56.72
30	13.39	77.20	50.81
31	05.99	68.87	44.73
32	44998.42	60.13	38.60
33	90.68	51.00	31.72
34	82.75	41.82	25.01
35	74.39	32.57	18.07
36	65.75	22.98	10.72
37	56.78	13.67	03.06
38	47.82	02.71	44995.58
39	37.98	892.20	87.36
40	27.83	81.56	79.02
41	21.97 12 67	70.76	70.65
42	12.67	59.57	61.97
43	01.33	47.94	52 92
44	890.61	36.59	43.52
45	79.69	24.80	34.09
46	68.69	12.54	25.16
47	57.42	00.31	14.87
48	45.86	787.53	03.76
49	34.04	74.75	894.20
50	23.16 17.16	61.36	85.37
51	09.69	48.35	82 47 70.76
52	796.44	34.50	53.51
53	94.51 81.01	32.66 19.83	41.42
54	73.73	698.58	26.46
55	61.36	83.70	14.35
56		66.81	01.62
57		52.00	789.51
58		36.01	75.77
59			63.88

TABLE 1 (Continued)
(4,0) band

J	$Q(J)$	$P(J)$	$R(J)$	J	$Q(J)$	$P(J)$	$R(J)$
3		45919.63		34	76.95	36.27	18.26
4		17.81		35	67.86	26.24	11.05
5	45921.00	15.25		36	58.24	15.77	03.28
6	19.63	12.53	45928.16	37	50.43	04.67	795.26
7	17.81	09.44	27.61		46.33		
8	15.83	06.41	26.82	38	42.46	695.41	86.98
9	13.60	03.20	25.77	39	31.95	84.45	78.45
10	11.43	899.24	24.61	40	21.62	74.46	68.84
11	08.33	95.34	22.64	41	11.19	62.52	61.74
12	05.16	91.11	21.00	42	01.37	51.37	51.39
13	01.85	86.77	19.10	43	690.55	39.41	41.45
14	898.27	81.78	16.82	44	79.38	26.60	32.42
15	94.08	77.19	14.34	45	67.85	14.28	22.92
16	90.77	71.99	11.43	46	56.44	02.56	12.09
17	86.50	66.46	08.33	47	44.58	588.90	01.37
18	82.11	60.71	05.85	48	32.54	75.97	690.55
19	78.26	55.01	01.85	49	19.88	63.08	79.38
20	73.15	49.14	898.27	50	07.64	48.07	68.00
21	68.01	42.25	94.82	51	594.81	32.87	56.44
22	62.46	35.61	89.51	52	81.63	19.93	44.58
23	56.70	28.74	84.82	53	68.35		32.54
24	50.64	21.68	80.24	54	54.84		19.88
25	44.46	14.27	75.28	55	40.79		07.64
26	37.94	06.76	70.14	56	26.77		594.81
27	31.24	798.07	64.56	57	12.45		81.63
28	24.29	90.35	58.66	58			68.35
29	17.13	81.75	52.62	59			54.84
30	09.65	73.23	46.41	60			40.79
31	01.82	64.46	39.83	61			26.77
32	793.92	55.40	32.90	62			12.45
33	85.59	46.33	25.53				

TABLE 1. (continued)

(4,1) band			(5,1) band			
J	$Q(J)$	$R(J)$	J	$Q(J)$	$P(J)$	$R(J)$
18	44656.98		16		45432.74	
19	50.97		17		27.45	
20	46.16	44670.50	18		21.59	
21	41.10	66.30	19		15.59	
22	35.86	62.95	20		08.97	45458.00
23	30.38	58.77	21	45428.49	03.34	54.04
24	24.60	54.06	22	22.46	396.38	49.63
25	18.56	49.23	23	16.72	89.61	44.49
26	12.37	44 17	24	09.96	82.33	40.22
27	06.00	38.93	25	04.48	74.22	34.93
28	599.04	33.67	26	397.84	66.94	29.40
29	92.24	27.79	27	90.87	58.85	23.89
30	85.04	21 99	28	83.84	50.51	18.00
31	77.57	15.60	29	70.47	41.73	11.77
32	70.03	09.13	30	68.75	33.36	05.69
33	61.97	02.28	31	61.13	24.38	398.95
34	53.61	595.24	32	53.29	15.16	92.04
35	44.99	88.26	33	44.61	05.61	85.12
36	35.65	81.09	34	36.20	295.82	77.43
37	31.62	73.15	35	27.42	85 93	69.86
	22.18		36	18.34	75.55	62.13
38	20.40	65.54	37	08.81	65.00	53.29
39	10.31	57.44	38	299.14	54.32	44.81
40	00.26	48.88	39	88.80	43 10	36.20
41	493.03	40.21	40	79.29	31.63	27.42
	90.16		41	68.95	20.65	18.34
42	80.98	31.62	42	58.21	08 49	08.81
43	70.35	28.32	43	47.38	196.69	299.14
		25.65	44	36 26	84.07	88.80
44	59.56	14.94	45	24.62	71.76	78.57
45	49.86	04.74	46	12.96	58.64	68.07
46	37.78	494.89	47	01.07	45.47	57.25
47	26.29	84.50	48	188.75	31.89	46.25
48	14.90		49	76.27		35.38
			50	63.29		23.80
			51	49 83		
			52	35.89		

The equality of combination differences $\Delta_2 F''(J)$ obtained for $v'' = 0$ level from different bands are collected in table 2 and the rotational constants

TABLE 2

Combination differences for bands having the same lower state $v''=0$

$$\Delta_2 F''(J) = R(J-1) - P(J+1)$$

J	(0,0) band	(2,0) band	(3,0) band	(4,0) band
7				21.75
8				24.59
9				27.48
10				30.43
11	33.35			33.50
12	36.80			35.87
13	39.69			39.22
14	41.75			42.00
15	44.58			44.83
16	47.94			47.88
17	50.34	50.38		50.72
18	53.66	52.95	53.67	53.32
19	56.19	56.04		56.02
20	58.48	59.27	59.23	59.60
21	62.19	62.10		62.66
22	65.16	66.21	64.66	66.08
23	68.01	67.91	67.46	67.83
24	70.86	70.92	70.42	70.55
25	73.64	73.88	73.55	73.48
26	76.79	76.48	76.92	77.21
27	79.59	80.24	79.64	79.79
28	82.33	82.75	83.06	82 81
29	85.65	85.37	86.08	85.43
30	88.06	87.97	87.85	88.16
31	90.86	91.16	90.68	91.01
32	93.91	93.92	93.73	93.50
33	96.68	96.96	96.78	96.63
34	99.78	99.68	99.15	99.29
35	102.57	102.96	102.03	102.49
36	105.52	105.52	104.40	106.38
37	108.44	108.41	108.01	107.87
38	111.57	111.27	110.86	110.86
39	113.70	113.57	114.02	112.52
40	116.40	116.20	116.60	115.93
41	119.93	119.23	119.45	119.47
42	122.75	122.32	122.71	122.33
43	125.28	124.94	125.38	124.70*
44	128.34	127.92	128.12	127.17*
45	131.46	130.78	130 98	129.86*
46	134.11	133.69	133.78	130.17*
47	136.83	136.71	137.63	135.67*
48	139.92	139.31	140.12	138.29*
49	142.17	142.31	142.40	142.48*
50	145.34	145.41	145.85	146.51
51	147.97	148.00	147.97	148.07
52	150.83	151.16	150.76	
53	153 87	153.70	154.93	
54		157.61		
55		159.47		
56		162.28		
57		165.50		

* Corresponding lines are very much diffused.

are collected in table 3. In the case of (4,1) band where only two series are detected the constant for the upper state was obtained by drawing $Q(J)$

TABLE 3. ROTATIONAL CONTENTS FOR THE ULTRAVIOLET BANDS OF SiO (in cm^{-1})

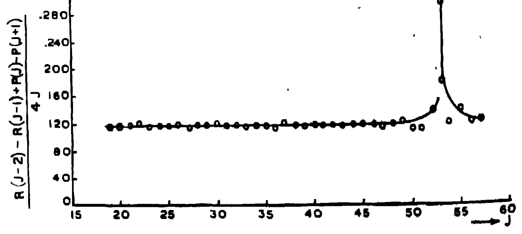
Band	$B''v$	$D''v \times 10^6$	$B'v$	ν_0
0,0	0.7246	1.02	0.6271	42640.75
2,0	0,7246	1.02	0.6122	44308.75
3,0	0.7246	1.02	0.6062	45124.00
4,0	0.7246	1.02	0.6002	45925.00
4 1	0 7195	1.00	0.6002	44696.75
5,1	0 7195	1.00	0.5925	45487.50
$B''_e = 0.7271\ cm^{-1}$			$r''_e = 1.508$ Å	
$B'_e = 0.6305\ cm^{-1}$			$r'_e = 1.619$ Å	

against $J(J+1)$ the slope of which gives the $\triangle B$ value. The B_4' value was obtained from the B_1'' value obtained from the analysis of (5,1) band. The $\triangle$-type doubling in the upper $^1\pi$ state was obtained frem the relation

$$[R(J-Q(J)] - [Q(J+1) - P(J+1)] = 2p(J+1)^2 \qquad (5)$$

and the value obtained is $B^d - B^c = p = -7\times10^{-5}\ cm^{-1}$.

A large number of perturbations in Q, R and P branches are observed. Perturbations were detected by using equations (3) and (4) and plotting the expressions on the left hand side against J (Lagerqvist & Uhler 1953, Lagerqvist *et al* 1958). The interesting feature is that perturbations are observed in Q as well as R and P branches at different J values which indicates that both the $\wedge$ levels of $^1\pi$ state are perturbed. The perturbation in some of the bands are represented in figure 2.



The authors wish to thank Prof. N L. Singh for his interest in the work and to Dr. D. K. Rai for valuable discussion. They are grateful to the National Bureau of Standards, U.S.A., and to the Council of Scientific and Industrial Research, India, for financial assistance.

REFERENCES

Gerö, L. 1935 *Z. Physik* **93**, 669.

Herzberg, G. 1950 *Spectra of Diatomic Molecules*, D. Von Nostrand & Co. Inc., New York.

Lagerqvist, A. & Uhler, U. 1953 *Ark. For Fysik* **6**, 95.

Lagerqvist, A., Westerlund, H., Wright, C. V. & Barrow. R. F. 1958 *Ark. For. Fysik* **14**, 387.

Saper, P. 1932 *Phys. Rev.* **42**, 498.

Verma, R. D. 1961 *Can. J. Phys.* **39**, 908.